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## GENERAL FORMALISM FOR SINGLY-THERMOSTATED HAMILTONIAN DYNAMICS

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### ABSTRACT

A general formalism is developed for constructing modified Hamiltonian dynamical systems which preserve a canonical equilibrium distribution by adding a time evolution equation for a single additional thermostat variable. When such systems are ergodic, canonical ensemble averages can be computed as dynamical time averages over a single trajectory. Systems of this type were unknown until their recent discovery by Hoover and colleagues. The present formalism should facilitate the discovery, construction, and classification of other such systems by encompassing a wide class of them within a single unified framework. This formalism includes both canonical and generalized Hamiltonian systems in a state space of arbitrary dimensionality (either even or odd), and therefore encompasses both few- and many-particle systems. Particular attention is devoted to the physical motivation and interpretation of the formalism, which largely determine its structure. An analogy to stochastic thermostats and fluctuation-dissipation theorems is briefly discussed.

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## I. INTRODUCTION AND SUMMARY

In the classical Hamiltonian dynamics of an isolated conservative system, the energy is a constant of the motion whose numerical value is simply the value of the Hamiltonian at the initial phase point. If such a system is ergodic, microcanonical ensemble averages at a given fixed energy can be computed as dynamical time averages over any single trajectory whose initial phase point lies on that energy surface. More often, however, one would rather compute canonical ensemble averages at a given fixed temperature, which implies a distribution of energies and a corresponding distribution of initial phase points. Canonical averages therefore cannot be computed as dynamical time averages over a single trajectory of the original Hamiltonian system. A great deal of research has been devoted to methods for modifying the Hamiltonian dynamics so that an entire canonical distribution can be sampled by following a single trajectory. Such modifications or models are commonly referred to as *thermostats*, which may be broadly characterized as stochastic or deterministic. The former have the advantage that they can draw upon the extensive body of methods and results that have evolved from the classical Langevin theory of Brownian motion [1–3]. Deterministic models are simpler and more reproducible, but they lack a well-established historical foundation analogous to the Langevin theory, so they have had to be developed *ab initio*. There was little or no motivation to pursue such a development prior to the advent of fast digital computers, so most of it has occurred during the past thirty years, beginning with the pioneering work of Nosé [4, 5].

In spite of its relatively brief history, the literature in this field has become voluminous. A bewildering variety of different deterministic models has by now been explored with mixed results. Fortunately, the most significant subset of this literature has now been reviewed in mono-

graphs [6–13], except of course for very recent developments. (The older books cited are now out of date as regards the state of the art, but they still contain very useful discussions of the fundamentals.) Our discussion here is therefore restricted to papers having direct relevance to the present development.

Hoover recognized that Nosé’s original model was needlessly complex, and transformed it into a greatly simplified form now referred to as Nosé-Hoover dynamics [14]. Unfortunately, it is insufficient for the dynamics to merely preserve a canonical equilibrium distribution, because this does not imply that the trajectory generated by an arbitrary initial phase point will sample the entire distribution. If it does not, the system is not ergodic, time and ensemble averages are not equivalent, and the system is not useful. Alas, ergodicity proofs for systems of practical interest are practically nonexistent, so in practice ergodicity or its absence must be determined beyond a reasonable doubt by numerical experiments. Such experiments revealed that the Nosé and Nosé-Hoover models are far from ergodic, and therefore cannot be used to compute canonical ensemble averages.

The Nosé-Hoover model is a singly-thermostated model; i.e., it is based on the time evolution of a single additional thermostat variable, which plays the role of a linear friction coefficient of indefinite sign that can be interpreted as controlling the mean kinetic energy of the system. It was soon discovered that ergodicity could be achieved by introducing various combinations of *non-linear* frictional and/or kinematic terms involving *two* thermostat variables [15–18]. Such models then became the state of the art, and remained so for the next quarter century or so. During this period numerous attempts were made to construct singly-thermostated ergodic models with canonical equilibrium distributions, but a persistent lack of success led to a growing suspicion that such models may not exist [19]. That suspicion was laid to rest by the surprising recent discovery of

several such models [20–22], which demonstrate by construction that a second thermostat variable is not necessary for ergodicity after all. What does appear to be essential is that the friction terms are nonlinear and not too simple in form, although they need not be any more complicated than those in the doubly-thermostated models [15–18]. Our purpose here is to present a compact general formalism which encompasses a wide variety of such models by incorporating their essential shared features into a unified framework. A primary emphasis is placed on the physical motivation and interpretation of the formalism, which largely determine its structure. The resulting general formulation can then readily be specialized to generate a wide variety of other similar models, thereby facilitating their discovery, development, and classification. The formalism includes both canonical and generalized Hamiltonian systems in a state space of arbitrary dimensionality  $n$ , so that it applies to both few- and many-particle systems with either integral or half-integral degrees of freedom (i.e., even or odd  $n$ ).

The generality of the present treatment should not be allowed to obscure the fact that it is based on the same basic physical ingredients that underlie most of the previous thermostated dynamical models cited above, namely

- (a) The use of generalized frictional terms to produce variations in the energy, which would otherwise remain constant.
- (b) Time-dependent friction coefficients (or “thermostat variables”) which alternate between positive and negative values, thereby producing alternating periods of decreasing and increasing energy, and deterministic energy fluctuations about a nonzero mean value.
- (c) Time evolution equations for the friction coefficients, the form of which must ensure that the resulting energy distribution is canonical with the desired specified temperature.

As will be seen, the structure of the present formalism is largely determined by these three essential ingredients.

Our starting point is a generalized formulation of Hamiltonian dynamics [23–25] which is more compact and easier to work with than the canonical form, to which it reduces as a special case. This dynamics conserves the energy of the system, so it must be modified to allow the energy to vary as required to sample the canonical distribution. The natural and obvious physical mechanism by which the energy can be varied is friction, which of course is the rationale for ingredient (a) above. It is convenient and natural to introduce friction into the generalized Hamiltonian dynamics by means of a generalized dissipative term of the form that appears in the “mixed canonical and dissipative dynamics” of Enz [26]. Ingredient (b) is then introduced by affixing a single time-dependent friction coefficient to the dissipative term. The simplest and most straightforward route to ingredient (c) is via the generalized Liouville equation [27–30], of which the canonical equilibrium distribution is required to be a steady-state solution [6, 14–17, 31]. Imposing this requirement leads directly to the required time evolution equation for the friction coefficient. This approach was systematically exploited by Kusnezov, Bulgac, and Bauer (KBB) [15–17], who presented a general framework for introducing generalized friction terms involving two independent thermostat variables into canonical Hamiltonian dynamics, and for inferring the time evolution equations those variables must satisfy to obtain consistency with a canonical equilibrium distribution. The present development proceeds in much the same spirit, but is considerably simpler due to our use of generalized Hamiltonian dynamics and a single thermostat variable. Of course, the KBB formulation was developed at a time when it was widely suspected that two or more thermostat variables are necessary to obtain ergodicity. In light of the recent evidence that a single such variable is sufficient [20–22], it seems worthwhile to focus attention on singly-thermostated models in greater detail and generality.

The remainder of the paper is organized as follows. The equations of motion for a generalized Hamiltonian system containing nonlinear frictional terms are developed in Sect. II. The friction terms are taken to be proportional to a single time-dependent scalar friction coefficient  $z(t)$ . A time evolution equation for  $z(t)$  is derived in Sect. III by requiring the canonical equilibrium distribution to be a stationary solution of the corresponding generalized Liouville equation. In Sect. IV the general formulation is specialized to canonical Hamiltonian dynamics in rectangular Cartesian coordinates, which is the most common case of interest. In Sect. V we specialize the canonical formulation to systems with a single degree of freedom, which provides a simple direct route to the recent models of Hoover et al. [21]. Section VI contains a few concluding remarks.

## II. GENERALIZED HAMILTONIAN DYNAMICS WITH FRICTION

Our starting point is an arbitrary unmodified Hamiltonian system of the general form [23–25]

$$\dot{\mathbf{x}} = \mathbf{A}(\mathbf{x}) \cdot \nabla H \quad (1)$$

where  $\mathbf{x} = (x_1, x_2, \dots, x_n)$  is the phase point,  $H(\mathbf{x})$  is the Hamiltonian function,  $\nabla \equiv \partial/\partial\mathbf{x}$ , and  $\mathbf{A}(\mathbf{x})$  is an antisymmetric matrix satisfying the condition

$$\nabla \cdot \mathbf{A} = 0. \quad (2)$$

The antisymmetry of  $\mathbf{A}$  implies at once that  $H$  is a constant of the motion; i.e.,  $\dot{H} = \dot{\mathbf{x}} \cdot \nabla H = 0$ . Equation (2) combines with the antisymmetry of  $\mathbf{A}$  to imply that  $\nabla \cdot (\mathbf{A} \cdot \nabla H) = 0$ , so that Eq. (1) generates an incompressible or volume-preserving flow in the phase space. Equation (1) is simpler,

more compact, and also more general than canonical Hamiltonian dynamics, to which it reduces as a special case as discussed in Sect. IV.

Next we add friction by introducing a dissipative term of the form used by Enz [26], so that Eq. (1) is replaced by

$$\dot{\mathbf{x}} = \mathbf{A}(\mathbf{x}) \cdot \nabla H - \mathbf{D}(\mathbf{x}) \cdot \nabla H \quad (3)$$

where the friction matrix  $\mathbf{D}(\mathbf{x})$  is symmetric and positive semidefinite. It then follows that

$$\dot{H} = - \nabla H \cdot \mathbf{D} \cdot \nabla H \leq 0 \quad (4)$$

so that the dissipative term produces a monotonic decay in the energy, as it was designed to do. The friction matrix  $\mathbf{D}$  therefore provides a convenient general framework for introducing artificial terms into the dynamics that possess a clear physical interpretation as analogs of real physical dissipative effects such as viscosity, friction, and drag. As discussed in the Introduction, however, in the present context it is necessary for the energy to alternate between periods of growth and decay so that it can generate a canonical energy distribution with a nonzero mean value. The obvious way to accomplish this is to simply multiply the dissipative term in Eq. (3) by a time-dependent dimensionless scalar friction coefficient  $z(t)$  which takes on both positive and negative values, so that the dissipation is reversed when  $z$  becomes negative. We thereby obtain

$$\dot{\mathbf{x}} = \mathbf{A}(\mathbf{x}) \cdot \nabla H - z \mathbf{D}(\mathbf{x}) \cdot \nabla H \equiv \mathbf{U}(\mathbf{x}, z) \quad (5)$$

from which it follows that  $\dot{H} = - z(t) \nabla H \cdot \mathbf{D} \cdot \nabla H$ , so that the energy increases when  $z(t) < 0$  and decreases when  $z(t) > 0$ . Since ordinary friction coefficients are positive, we shall refer to

$z(t)$  as a generalized friction coefficient, which serves as a reminder that it will alternate between positive and negative values, and that it is affixed to a generalized dissipative term of the form  $\mathbf{D} \cdot \nabla H$ . It will also be referred to as a (or in this case the) thermostat variable, in accordance with common usage in molecular dynamics.

Although  $\mathbf{D}$  is normally positive semidefinite in real physical systems, one might inquire why we continue to impose that requirement in the present context, since multiplying  $\mathbf{D}$  by  $z$  produces a matrix of indefinite sign. The rationale for retaining this requirement is to preserve as much as possible of our physical intuition about the qualitative behavior of frictional terms, and to force the variable  $z$  to carry the entire burden of reversing the sign of such terms. However, this is not an absolute requirement, and it would not be inconsistent to consider models in which it is relaxed. However, if this were done the sign of  $\dot{H}$  could no longer be determined from  $z$  alone.

Of course, Eq. (5) does not represent the most general possible way of introducing a single thermostat variable into the friction term. A much more general form would be obtained by replacing  $z\mathbf{D}(\mathbf{x})$  by  $\mathbf{F}(z) \cdot \mathbf{D}(\mathbf{x})$  in Eq. (5), where  $\mathbf{F}(z)$  is a symmetric matrix each of whose elements is a function of  $z$ . However, that level of complexity is unmanageable (except in small simple systems) and would make it practically impossible to preserve a clear physical interpretation of the formalism, and to anticipate the qualitative behavior of the dynamics based on physical intuition and insight.

One might wonder if it would at least be useful to replace  $z$  by a scalar function  $F(z)$  in Eq. (5), with the understanding that  $F(z)$  would likewise need to assume both positive and negative values. This apparent additional generality would be specious and illusory, however, since  $\dot{F} = (dF/dz) \dot{z}$ , so the time evolution of  $z$  defines and determines the time evolution of  $F(z)$ , and



vice versa. Specifying the former is therefore equivalent to specifying the latter, so replacing  $z$  by  $F(z)$  is tantamount to simply denoting  $z$  by the different symbol  $F$ .

### III. THE TIME EVOLUTION OF THE FRICTION COEFFICIENT

The time evolution of  $z$  is not known or specified *a priori*, so it must be determined by considering  $z$  as an additional dynamical variable. The enlarged state space of the system then becomes  $(\mathbf{x}, z)$ , and in order for the system to remain deterministic and autonomous  $z$  must obey a time evolution equation of the form

$$\dot{z} = W(\mathbf{x}, z) \quad (6)$$

which together with Eq. (5) determines the time evolution of the system. It is now necessary to determine what form the function  $W(\mathbf{x}, z)$  must have in order for the dynamics to generate a canonical distribution in the energy. Fortunately, this need not be done by trial and error but can be accomplished in a systematic way simply by requiring a canonical distribution with a specified temperature to be a stationary solution of the generalized Liouville equation [27–30], which in the present context takes the form

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{U}) + \frac{\partial(\rho W)}{\partial z} = 0 \quad (7)$$

where  $\rho(\mathbf{x}, z, t)$  is the normalized probability distribution in the variables  $(\mathbf{x}, z)$  at time  $t$ . The form of  $W$  is constrained by the requirement that Eq. (7) must possess a steady (time-independent) solution  $\rho_s(\mathbf{x}, z)$  whose reduced distribution in  $\mathbf{x}$  alone is canonical; i.e.,

$$\int dz \rho_s(\mathbf{x}, z) = \rho_c(\mathbf{x}) \equiv Q^{-1} \exp\{-\beta H(\mathbf{x})\} \quad (8)$$

where  $\beta = 1/T$ ,  $T$  is the specified temperature in energy units, and  $Q(\beta) \equiv \int d\mathbf{x} \exp\{-\beta H(\mathbf{x})\}$  is the canonical partition function. The simplest way to satisfy Eq. (8) is to require that  $\mathbf{x}$  and  $z$  be statistically independent in steady state, so that

$$\rho_s(\mathbf{x}, z) = \rho_c(\mathbf{x}) \sigma(z) \quad (9)$$

where  $\sigma(z)$  is nonnegative and satisfies  $\int dz \sigma(z) = 1$ , but is otherwise as yet undetermined.

Combining Eqs. (5) and (7)–(9), we obtain, after a little algebra,

$$\nabla \cdot (\mathbf{D} \cdot \nabla H) - \beta \nabla H \cdot \mathbf{D} \cdot \nabla H = \frac{1}{z\sigma} \frac{\partial(\sigma W)}{\partial z} \quad (10)$$

where use has been made of Eq. (2) and the antisymmetry of  $\mathbf{A}$ . Even if  $\sigma(z)$  were given or known, Eq. (10) obviously does not uniquely determine  $W$ , because it leaves  $\sigma W$  undetermined to within an arbitrary function of  $\mathbf{x}$ . This nonuniqueness affords us the freedom to restrict attention to functions  $W(\mathbf{x}, z)$  of the separable form

$$W(\mathbf{x}, z) = \varphi(z) \chi(\mathbf{x}) \quad (11)$$

so that Eq. (6) becomes

$$\dot{z} = \varphi(z) \chi(\mathbf{x}) \quad (12)$$

The function  $\varphi(z)$  provides a mechanism whereby the rate at which the generalized friction coef-

ficient  $z(t)$  responds to  $\mathbf{x}$  can be either accelerated or retarded based on the value of  $z$  itself, which is a potentially useful feature. It is clear, however, that  $\varphi(z)$  should not be allowed to change the sign of  $\dot{z}$ , since whether  $z$  needs to increase or decrease to maintain a canonical distribution in  $\mathbf{x}$  is determined entirely by  $\mathbf{x}$ . Thus  $\varphi(z)$  cannot change sign, and we can require  $\varphi(z) > 0$  with no loss in generality. Equation (10) now becomes

$$\frac{1}{\chi(\mathbf{x})}[\nabla \cdot (\mathbf{D} \cdot \nabla H) - \beta \nabla H \cdot \mathbf{D} \cdot \nabla H] = \frac{1}{z\sigma} \frac{d(\sigma\varphi)}{dz} \quad (13)$$

The left member of Eq. (13) depends only on  $\mathbf{x}$ , while the right member depends only on  $z$ , so they must both have the same constant value, which we denote by  $-1/\alpha$ . It follows that

$$\chi(\mathbf{x}) = \alpha[\beta \nabla H \cdot \mathbf{D} \cdot \nabla H - \nabla \cdot (\mathbf{D} \cdot \nabla H)] \quad (14)$$

and

$$\alpha \frac{d(\sigma\varphi)}{dz} = -z\sigma \quad (15)$$

Equation (15) implies that  $\alpha$  must be positive, for if it were negative  $\sigma$  would not in general be normalizable, as shown by the special case  $\varphi = 1$ , in which the solution of Eq. (15) is  $\sigma(z) = \sigma(0) \exp\{-z^2/(2\alpha)\}$ . It follows that the factors of  $\alpha$  in Eqs. (14) and (15) can simply be absorbed into the positive quantities  $\mathbf{D}$  and  $\varphi$ , which is formally tantamount to simply setting  $\alpha = 1$ . Equations (14) and (15) then simplify to

$$\chi(\mathbf{x}) = \beta \nabla H \cdot \mathbf{D} \cdot \nabla H - \nabla \cdot (\mathbf{D} \cdot \nabla H) \quad (16)$$

$$\frac{d(\sigma\varphi)}{dz} = -z\sigma \quad (17)$$

Equation (16) explicitly determines  $\chi(\mathbf{x})$ , while Eq. (17) is an ordinary differential equation which relates  $\sigma(z)$  and  $\varphi(z)$ . One of those functions can be chosen at will (subject to the aforementioned constraints) and Eq. (17) then determines the other. The functional form of  $\sigma(z)$  is essentially immaterial, since it has no effect on the canonical equilibrium distribution  $\rho_c(\mathbf{x})$ , whereas  $\varphi(z)$  directly affects the dynamics via Eq. (12). It is therefore natural to regard  $\varphi(z)$  as a specified function, which then determines  $\sigma(z)$  via Eq. (17). Equation (17) can be rewritten as

$$\frac{d}{dz} \log(\sigma\varphi) = -\frac{z}{\varphi} \quad (18)$$

which can immediately be integrated to obtain

$$\sigma(z) = \frac{C}{\varphi(z)} \exp \left\{ -\int_0^z \frac{s ds}{\varphi(s)} \right\} \quad (19)$$

where  $C$  is a constant of integration. Equation (19) provides an explicit expression for  $\sigma(z)$  for a given  $\varphi(z) > 0$ . The constant  $C$  is not arbitrary or unknown, because it is simply determined by the normalization condition  $\int dz \sigma(z) = 1$ . In the special case  $\varphi(z) = 1$ , Eq. (19) reduces to

$$\sigma(z) = C \exp\left\{-\frac{1}{2}z^2\right\} \quad (20)$$

where  $C = 1/\sqrt{2\pi}$ , so the steady-state distribution in  $z$  is Gaussian in this case, with a variance of  $\langle z^2 \rangle = \int dz z^2 \sigma(z) = 1$ .

According to Eqs. (12) and (16),  $\dot{z}$  is proportional to  $\mathbf{D}$ , and as previously noted  $\dot{H} = -z(t)\nabla H \cdot \mathbf{D} \cdot \nabla H$  is likewise proportional to  $\mathbf{D}$ . It follows that the time scales for the dynamical evolution of both  $z$  and  $H$  can be made shorter simply by making  $\mathbf{D}$  larger (e.g., multiplying it by a dimensionless scalar coefficient  $> 1$ ), which would therefore be expected to produce a faster approach to the steady-state distribution and faster asymptotic convergence of time averages. Beyond a certain point, however, shorter time scales result in stiffness and numerical inefficiency, and in any case it seems pointless to make the time scales associated with  $\mathbf{D}$  any shorter than those associated with  $\mathbf{A}$  in the original Hamiltonian system of Eq. (1), which also limit the rate of approach to a steady-state distribution. Ideally it would be preferable for all the various time scales to be of the same order of magnitude, so in practice it may be advantageous to rescale or renormalize  $\mathbf{D}$  to that end, which will require numerical experimentation.

The general formalism is now complete. The dynamical evolution of the phase point  $(\mathbf{x}, z)$  is determined by Eqs. (5) and (12), in which  $\chi(\mathbf{x})$  is given by Eq. (16). The function  $\varphi(z) > 0$  and the positive semidefinite matrix  $\mathbf{D}$  may be chosen at will. By construction, any dynamical system of this form will preserve a steady-state probability distribution of the canonical form (9), where  $\rho_c(\mathbf{x})$  and  $\sigma(z)$  are given by Eqs. (8) and (19), and if the system is ergodic it will dynamically generate that distribution as  $t \rightarrow \infty$  starting from almost all initial phase points  $(\mathbf{x}_0, z_0)$ .

#### IV. CANONICAL HAMILTONIAN SYSTEMS

Here we specialize the general formalism to canonical Hamiltonian systems with  $f$  degrees of freedom, for which  $n = 2f$  is even. For a system of  $N$  point particles in  $d$ -dimensional space,  $f = Nd$ . We now have  $\mathbf{x} = (\mathbf{q}, \mathbf{p})$  and  $\nabla H = (\partial H / \partial \mathbf{q}, \partial H / \partial \mathbf{p})$ , where  $\mathbf{q} = (q_1, \dots, q_f)$  and

$\mathbf{p} = (p_1, \dots, p_f)$  are the canonical coordinates and momenta. The canonical form of the matrix  $\mathbf{A}$  is

$$\mathbf{A} = \begin{bmatrix} \mathbf{0} & \mathbf{1} \\ -\mathbf{1} & \mathbf{0} \end{bmatrix} \quad (21)$$

where  $\mathbf{0}$  and  $\mathbf{1}$  are the zero and unit  $f \times f$  matrices, respectively. It then follows that  $\mathbf{A} \cdot \nabla H = (\partial H / \partial \mathbf{p}, -\partial H / \partial \mathbf{q})$ , whereupon Eq. (1) immediately yields the canonical Hamiltonian equations of motion  $\dot{\mathbf{q}} = \partial H / \partial \mathbf{p}$  and  $\dot{\mathbf{p}} = -\partial H / \partial \mathbf{q}$ .

We shall restrict attention to conservative systems in rectangular Cartesian coordinates, in which  $H(\mathbf{q}, \mathbf{p})$  assumes the familiar form

$$H(\mathbf{q}, \mathbf{p}) = \frac{1}{2}|\mathbf{p}|^2 + V(\mathbf{q}) \quad (22)$$

where  $V(\mathbf{q})$  is the potential energy, and all particle masses have been set equal to unity for simplicity. It follows that  $\partial H / \partial \mathbf{q} = \partial V / \partial \mathbf{q}$  and  $\partial H / \partial \mathbf{p} = \mathbf{p}$ , so that  $\nabla H = (\partial V / \partial \mathbf{q}, \mathbf{p})$  and Eq. (1) immediately reduces to the Newtonian equations of motion

$$\dot{\mathbf{q}} = \mathbf{p} \quad (23)$$

$$\dot{\mathbf{p}} = -\frac{\partial V}{\partial \mathbf{q}} \quad (24)$$

In the present context, the friction matrix  $\mathbf{D}$  is of the general form

$$\mathbf{D}(\mathbf{q}, \mathbf{p}) = \begin{bmatrix} \mathbf{D}_q(\mathbf{q}, \mathbf{p}) & \mathbf{D}_\Delta(\mathbf{q}, \mathbf{p}) \\ \mathbf{D}_\Delta^\top(\mathbf{q}, \mathbf{p}) & \mathbf{D}_p(\mathbf{q}, \mathbf{p}) \end{bmatrix} \quad (25)$$

where  $\mathbf{D}_q$  and  $\mathbf{D}_p$  are symmetric, whereas  $\mathbf{D}_\Delta$  need not be, and superscript T denotes the transpose. According to Eq. (5), the matrices  $\mathbf{D}_q$  and  $\mathbf{D}_\Delta$  will have the effect of introducing generalized frictional terms into Eq. (23). Such terms have indeed frequently been employed in previous thermostat models (e.g., [16]), but they seem undesirable if not hazardous on the grounds that Eq. (23) is essentially kinematical in nature, so tampering with it is conceptually incongruous and may tend to confound our physical intuition. To forestall this danger, we shall simply set  $\mathbf{D}_q = \mathbf{D}_\Delta = \mathbf{0}$ , so that Eq. (25) reduces to

$$\mathbf{D}(\mathbf{q}, \mathbf{p}) = \begin{bmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{D}_p(\mathbf{q}, \mathbf{p}) \end{bmatrix} \quad (26)$$

It then follows that  $\mathbf{D} \cdot \nabla H = (\mathbf{0}, \mathbf{D}_p \cdot \mathbf{p})$ , so that Eq. (5) reduces to

$$\dot{\mathbf{q}} = \mathbf{p} \quad (27)$$

$$\dot{\mathbf{p}} = -\frac{\partial V}{\partial \mathbf{q}} - z \mathbf{D}_p \cdot \mathbf{p} \quad (28)$$

in which it is obvious that the term involving  $\mathbf{D}_p$  is a friction term, which is generally nonlinear due to the dependence of  $\mathbf{D}_p$  on  $(\mathbf{q}, \mathbf{p})$ . This term still preserves a great deal of generality, since it allows for frictional couplings between different degrees of freedom. This is probably much more generality than is necessary for practical purposes, so we shall adopt the further simplification that  $\mathbf{D}_p$  is diagonal with the form  $\mathbf{D}_p = [\delta_{ij} \gamma_i(q_i, p_i)]$ , where  $[a_{ij}]$  denotes the matrix whose  $(i, j)$  element is  $a_{ij}$ ,  $\delta_{ij}$  is the Kroencker delta, and  $\gamma_i \geq 0$  so that  $\mathbf{D}_p$  is positive semidefinite. Equation (28) then becomes

$$\dot{p}_i = -\frac{\partial V}{\partial q_i} - z \gamma_i(q_i, p_i) p_i \quad (29)$$

Notice that this form still preserves the dependence of the friction term on  $q_i$ , and thereby provides the option to localize the thermostating in coordinate space. Thus, for example, it could be restricted to regions at or near the boundaries of a finite region.

All that remains is to specialize the equation of motion for  $z(t)$  to the present situation, which merely requires us to evaluate the quantities in Eq. (16) and combine the result with Eq. (12).

We readily find that

$$\nabla H \cdot \mathbf{D} \cdot \nabla H = \mathbf{D}_p : \mathbf{p}\mathbf{p} = \sum_i \gamma_i p_i^2 \quad (30)$$

and

$$\nabla \cdot (\mathbf{D} \cdot \nabla H) = \frac{\partial}{\partial \mathbf{p}} \cdot (\mathbf{D}_p \cdot \mathbf{p}) = \sum_i \frac{\partial(\gamma_i p_i)}{\partial p_i} \quad (31)$$

Equations (12), (16), (30), and (31) then combine to yield

$$\dot{z} = \varphi(z) \sum_i \left( \beta \gamma_i p_i^2 - \frac{\partial(\gamma_i p_i)}{\partial p_i} \right) \quad (32)$$

in which  $\varphi(z) > 0$  can be chosen at will. We emphasize that the number of degrees of freedom  $f$  remains arbitrary, so these equations apply to both small and many-particle Hamiltonian systems. It is noteworthy that for this class of models, the time evolution equation (32) for  $z(t)$  is entirely independent of the form of the potential  $V(\mathbf{q})$ .



## V. SYSTEMS WITH A SINGLE DEGREE OF FREEDOM

A considerable portion of the previous work on thermostated dynamics has restricted attention to systems with a single degree of freedom, both because of their intrinsic theoretical interest and in order to gain insight into various alternative types of thermostated dynamics in situations which are more easily comprehensible and less computationally demanding. It is therefore of interest to specialize the above development to systems with only a single degree of freedom, for which  $\mathbf{x} = (q, p)$  and  $H = \frac{1}{2}p^2 + V(q)$ . Equations (27), (29), and (32) then immediately reduce to

$$\dot{q} = p \tag{33}$$

$$\dot{p} = -\frac{dV}{dq} - z\gamma p \tag{34}$$

$$\dot{z} = \varphi(z) \left( \beta\gamma p^2 - \frac{\partial(\gamma p)}{\partial p} \right) \tag{35}$$

As previously noted, Eq. (35) is independent of the form of  $V(q)$ . For simplicity we further restrict attention to models in which  $\gamma = \gamma(p)$  is independent of  $q$ , so that Eq. (35) reduces to

$$\dot{z} = \varphi(z) \left( \beta\gamma p^2 - \frac{d(\gamma p)}{dp} \right) \tag{36}$$

The simplest choices for  $\varphi(z)$  and  $\gamma(p)$  are  $\varphi = 1$  and a constant  $\gamma$  independent of  $p$ . With those choices, Eq. (36) becomes

$$\dot{z} = \gamma(\beta p^2 - 1) \tag{37}$$

For a one-dimensional simple harmonic oscillator with  $V = \frac{1}{2}q^2$ , Eqs. (33), (34), and (37) reduce

to the Nosé-Hoover model [14] (with  $\zeta = \gamma z$ ). It is reassuring to see this model emerge so easily as a simple special case of the general formalism.

Numerous detailed studies have confirmed that the Nosé-Hoover model is not ergodic; it is evidently insufficiently nonlinear. Subsequent studies showed that friction terms nonlinear in  $p$  are conducive to ergodicity [16, 20, 21, 31]. Since  $\gamma(p) > 0$ , the simplest such terms are obtained by letting  $\gamma(p)$  be a low-order polynomial in the dimensionless variable  $\beta p^2$  with positive coefficients. Thus we are led to consider

$$\gamma(p) = a + b\beta p^2 + c\beta^2 p^4 \quad (38)$$

which combines with Eqs. (34) and (36) to yield

$$\dot{p} = -\frac{dV}{dq} - z(ap + b\beta p^3 + c\beta^2 p^5) \quad (39)$$

$$\dot{z} = \varphi(z)[a(\beta p^2 - 1) + b(\beta^2 p^4 - 3\beta p^2) + c(\beta^3 p^6 - 5\beta^2 p^4)] \quad (40)$$

If we transform variables by letting  $z = \zeta^\nu$  (where  $\nu$  is a positive integer which must be odd so that  $z$  can change sign) and set  $\varphi(z) = dz/d\zeta = \nu\zeta^{\nu-1} = \nu z^{1-1/\nu}$ , Eqs. (39) and (40) become

$$\dot{p} = -\frac{dV}{dq} - \zeta^\nu(ap + b\beta p^3 + c\beta^2 p^5) \quad (41)$$

$$\dot{\zeta} = a(\beta p^2 - 1) + b(\beta^2 p^4 - 3\beta p^2) + c(\beta^3 p^6 - 5\beta^2 p^4) \quad (42)$$

which is precisely a model recently discovered and analyzed by Hoover, Hoover, & Sprott (HHS) [21] for the cases of a harmonic oscillator ( $V = \frac{1}{2}q^2$ ) and pendulum ( $V = -\cos q$ ), in both of which the model appears to be ergodic for certain values of  $(a, b, c)$ . The steady-state probability distribution in  $\zeta$  is easily obtained by using Eq. (19) to evaluate  $\sigma(z)$  and transforming it to the

variable  $\zeta$  (which of course requires multiplication by the Jacobian  $dz/d\zeta$ ). When this is done the result is found to be  $C \exp\{-\zeta^{\nu+1}/(\nu+1)\}$ , in agreement with HHS. It is satisfying to see how the present formalism leads naturally to the HHS model in a very straightforward way.

During the evolution of thermostated dynamical models over the past thirty years, it has been found useful and insightful to interpret thermostat variables like  $z$  as integral control variables, and to interpret terms of the form appearing in Eq. (40) as controlling the moments of the probability distribution [6,13,18,20,21]. In the present development, however, such interpretations are merely ancillary and no longer guide the construction of the models, since the dependence of  $\dot{z}$  on  $\mathbf{x}$  is entirely determined by the assumed form of the friction terms via Eqs. (12) and (16). There seems no *a priori* reason to restrict attention to frictional terms of polynomial form, so it may be worthwhile to explore the behavior of other nonlinear functions; e.g.,  $\gamma(p) = a \cosh(b\sqrt{\beta} p)$ .

## VI. CONCLUDING REMARKS

The generalized Hamiltonian formalism on which the present development is based was previously used as a framework for introducing multiplicative noise and nonlinear dissipation into Hamiltonian dynamics in such a way as to preserve a canonical equilibrium distribution [25]. The resulting nonlinear Langevin equation can be regarded as a stochastic thermostat, of which the present development constitutes a close deterministic analog. In the Langevin theory, the noise and dissipation are represented by separate additive terms with nonlinear coefficients, which are related by a fluctuation-dissipation theorem. In the present development, the deterministic function  $z(t)$  plays somewhat the same role as the random noise in the stochastic theory, but is combined with the friction into a single purely multiplicative term  $z(t) \mathbf{D} \cdot \nabla H$  of indefinite sign. Thus the stochastic

and deterministic formulations differ somewhat in structure, but they share the common feature that their respective time-dependent forcing functions are self-consistently determined by requiring the resulting steady-state probability distribution in  $\mathbf{x}$  to be canonical. In the stochastic theory that requirement leads to the nonlinear fluctuation-dissipation theorem, while in the deterministic theory it leads to the relation between  $z(t)$  and  $\mathbf{D}$  given by Eqs. (12) and (16). The latter relation therefore constitutes a deterministic analog of the stochastic fluctuation-dissipation theorem, so it seems natural to regard and refer to it as a *deterministic fluctuation-dissipation (DFD) theorem*.

Finally, we remark that the general formalism of Sects. II and III could be extended if desired, at the cost of some additional complexity, to accommodate multiply-thermostated models with two or more friction coefficients  $(z_1(t), z_2(t), \dots)$ . This could be done simply by inserting factors of  $z_\mu$  ( $\mu = 1, 2, \dots$ ) into the individual elements of the matrix  $\mathbf{D}$  in Eq. (3), but it seems preferable to first determine the orthogonal matrix  $\mathbf{M}(\mathbf{x})$  which diagonalizes  $\mathbf{D}$ , so that  $\mathbf{D} = \mathbf{M} \cdot [\gamma_i \delta_{ij}] \cdot \mathbf{M}^T$ , where the  $\gamma_i(\mathbf{x})$  are the nonnegative eigenvalues of  $\mathbf{D}$ . Any or all of the nonzero  $\gamma_i(\mathbf{x})$  could then be multiplied by factors of  $z_\mu$  as desired, and the result combined with Eq. (3) to obtain a multiply-thermostated generalization of Eq. (5).

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